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Porosity and Oil Absorption Properties of Metal Compacts of Copper - Tin - Graphite

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A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
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PRINCIPLES OF POWDER METALLURGY

Powder metallurgy, the most recent innovation in metallurgical process, is not a new art; although not until recently did it become a matter of general interest, this being due not only to the products formed but also to the possibilities of future developments. The manufacture and application of metal powders is now beginning to take a position as a recognized part of the science of metallurgy.

The ancients practiced powder metallurgy of a kind[40*], but the earliest literature did not appear until the early part of the nineteenth century when Wallaston in 1828 brought out a paper describing his method for producing ductile platinum[6]. His method, however, was discarded soon after, due to improvements in furnace efficiency so that higher temperatures and a better control of furnace atmosphere were readily obtainable.

The invention of the incandescent lamp and the search for a process for producing tungsten in a ductile form led to the first commercial application of powder metallurgy. Here was a product for which there was an immediate and urgent demand[8]. The production of filament wire resulted in a familiarity with the process which later led to the discovery of other valuable metal powder products.

Comstock[9] has listed four principal products manufactured

*Numbers refer to bibliography entries.

in quantity from metal powders:

1. The refractory metals such as tungsten, tantalum and molybdenum.
2. Electric contact and electrode materials.
3. Porous bearings.
4. Hard cemented carbides used in tools and dies.

All of these products display strikingly unusual characteristics, and each has been responsible for a notable advance in the field of its particular application.

Barclay[4] suggests "powder metallurgy is also opening up an entirely new field, since we can now look forward to producing by this method alloys which are either wholly, or at least partly, immiscible in the liquid state."

In discussing powder metallurgy, the production of metal powders, of course, presents a primary aspect. This, in itself, constitutes a very important field of research, and limitation in the production of these powders will limit the possibilities in the field of powder metallurgy. It is not necessary that a metal be powdered by any one method nor does it necessarily follow that the metal powder of the same metal made by different methods will have the same physical properties.

Noel, Shaw, and Gebert[3] classify the methods of pulverizing metals as follows:

1. Machining
2. Milling--ball mills, stamps, attrition, etc.

3. Shotting--pouring liquid metal into water, through air, a gas, etc.
4. Atomizing--disintegrating by steam, compressed air, etc.
5. Granulation--stirring a molten metal while it is solidifying.
6. Condensation of metal vapors.
7. Reduction of oxide powders.
8. Chemical precipitation.
9. Electrolytic deposition.
10. Sintering--for producing alloy powders.
11. Formation of a powder from an alloy by dissolving or otherwise removing one of the alloy constituents.

These processes are becoming highly technical and exacting in order to comply with consumer's specifications in respect to such characteristics as particle size distribution, particle shape, flow factor, loading weight, chemical analysis, and electrical properties. One principal characteristic is the large surface area for a given weight of material. The metallurgical problems therefore become involved with surface phenomena to such a degree that they may be the most important controlling factors in the success of the process[27], and the effect of absorbed gases, chemical film formation, surface tension, vapor pressure, relation of voids to size and shape of material, and flow of fine aggregates under pressure are some of the problems to be investigated.

Compacts, the product of compression of powdered metals in molds, may be made in automatic machines requiring little attention or in machines requiring constant attention. Pressures used may vary from a few thousand pounds to over one hundred tons per square inch, the lower pressures being used where a porous compact is desired. The machines used in compressing the powders may be hydraulic, cam-operated or knuckle-operated and may have one, or more than one, die. To eliminate the difficulties arising from entrapped gases, the compressive force should be steadily and rapidly applied and the total compressive effort exerted in one movement. The resulting compacts can be controlled within amazingly narrow limits, and by striking the sintered piece this accuracy can be further increased to limits within .001 inch[6].

There is a wide divergence of opinion concerning the temperature at which the heat treatment should be carried out. This temperature may be above the melting point of one constituent and below that of another, but no doubt the pressure used in making the compact, the size of the powder particles, the method of heating, the degree of coalescence, and the final uniformity desired, are all factors. There are no fixed rules by which the proper temperature can be predetermined, so that experimental work is necessary to find the correct sintering temperature to make a product of the required physical properties.

Patch[34] points out that although it is possible experimentally to make certain types of metal powders, the economical manufacture of these products in quantity is impossible, thus limiting their commercial application. Some factors affecting the type of product that can be made are: (1) the objects must necessarily be small, due to the high pressures involved; (2) powders do not flow freely, making the manufacture of objects with reentrant angles practically impossible; (3) whatever must be made should be made in large quantities; (4) although some eccentricity would be allowed, concentricity must be considered; (5) relationship of machining costs and metal powder costs must be kept in mind.

Powder metallurgy may be advantageously used under the following conditions: (1) where a very hard alloy is required; for example, the cemented tungsten carbides; (2) where metals are difficult to melt such as tungsten, molybdenum and columbium; (3) where controlled porosity is desired; (4) where metals are immiscible as liquids and have widely separated melting points; (5) where exact proportions of the constituents are required; (6) where non-metals and metals must be used together in intimate contact; (7) where dimensions must be kept within narrow limits; (8) where conventional methods are more costly. As for the products made, if one mentioned nothing more than the cemented tungsten carbides and porous bearings, that would be sufficient justification for the important part powder metallurgy is playing in industry today.

NATURE OF THE BONDING ACTION

In a discussion of powder metallurgy, the question at once arises as to the nature of the bonding action which takes place between the metal particles. This question is of the utmost importance in a scientific approach to the process. The physical properties of the products formed depend upon the final characteristics of the particles of which it is composed as well as upon the nature of the bond. The particle and the bond are therefore the two most fundamental considerations of this art.

Comstock[8] discusses particle bonding of two general types as being possible:

1. A bond resulting from the cementing action of a constituent which is molten at some stage of the operation.

2. Particle-to-particle adhesion without melting, closely resembling intercrystalline bonding of cast metals.

The most important and almost exclusive example of the first type is furnished by the hard cemented carbides.[32] The formation of a liquid cementing medium as for example, cobalt, in the cemented carbides, is a more or less positive action. Its effects are largely understandable and can therefore be anticipated to a certain extent. If the liquid which is formed alloys with the major unmelted component, or has a tendency to dissolve it even slightly, it fulfills the requirements for capillary action and is distributed in its molten state by that method throughout the mass of the un-

dissolved powder particles. Two strongly limiting conditions, however, must be recognized as affecting this method: (1) The liquid formed must be in a very minor proportion or a badly segregated melt would result; (2) particle size must be carefully regulated or the liquid becomes saturated too soon by dissolving the easily assimilated smaller particles, and when this occurs, it can then no longer fulfill the requirements that were previously responsible for the complete distribution and bonding action, so that a material of low strength results. Powder products that require the formation of a liquid binder must therefore be limited to materials that can be satisfactorily composed of a large preponderance of a very carefully sized component.[9]

Bonding ofthe second type, that is, particle-to-particle adhesion without the formation of a self-distributing molten binder is not fully understood nor is their exact character discernible by observation of the final product. Two favorable conditions affect this type of metal powder fabrication: (1) Compositions of this type do not require the presence of a major proportion of any single component; their physical properties may therefore be varied widely in comparison to those that must consist of a preponderance of one material; (2) within limits, an affinity between components is apparently not essential.

The simplest conception of bonding is that the compacting pressure causes the particles to deform and interlock with each

other to produce a mechanical bond. Comstock[7] believes that the pressing action has brought the particle surfaces into intimate contact and has disrupted grains and crystal lattices. This is equivalent to cold working the individual particles and thus lowering the temperature at which recrystallization takes place. Thus the temperature at which a definite bonding action occurs is also lowered. This accounts for the relatively lower temperatures dealt with in powder metallurgy. Hardy[19] suggests that the friction developed during compression between the surface of one particle and the surface of another generates enough heat to weld the two surfaces together. Even though the welding may be confined to the surface, it is nevertheless important because it forms the starting point for diffusion which can take place only when there are clean metal surfaces in contact with each other. Balke[3] in discussing the bonding mechanism, states that it appears as though the surface tension of a solid is the prime factor in causing consolidation and is therefore the best aid in obtaining a piece of metal. Elevated temperatures, as during sintering, simply allow surface tension to operate in a reasonable time.

Bonding by means of diffusion and the subject of diffusion itself has produced much contradictory literature. Mehl[30] and Dorn and Harder[13] have written exhaustive papers on the subject of diffusion in solid metals. Since most of the experimental work on bonding and diffusion has been

done on massive metals and large surfaces in contact, further research will be necessary for the solving of problems of bonding in the smaller products of powder metallurgy.

POROSITY

The manipulation of metal powders permits the formation of unusual structural effects which it would not be feasible to produce by ordinary casting. The porous metal bearing is an outstanding example of this fact and is one of the most important and far reaching of the present applications of powder metallurgy.[9] In these products porosity is desirable for three reasons: first, to improve the mechanical performance of a bearing; second, to act as a reservoir for lubricating oil; and third, to provide a device independent of mechanical means for a continual supply of oil to the lubricating surface.

Porosity or the volume of voids in a compact is generally expressed as a percentage of the total volume of the compact. Goetzel[15] states that there are two types of porosity in sintered compacts. The first kind, which may be called "primary" porosity can be controlled to a certain extent by changing basic conditions such as type and particle size of powders and compacting pressure. The cavities produced are generally angular and more or less continuous. The other type, which may be called "secondary" porosity is developed during the heat treatment because of gas evolution and is influenced chiefly by two conditions: (1) the particle size of the powder and (2) type of heat treating atmosphere.

Influence of Forming Pressure on Porosity.

The influence of external pressure applied on a powder mass is:

1. To reduce porosity by movement of the particles into voids.
2. To reduce porosity by deformation of particles so that they key into each other.
3. To reduce porosity on an atomic scale by the flattening of the microscopic and submicroscopic asperities on the particle surface[23].

These processes result in a considerable increase in the total contact area and therefore in the cold sintered strength of the body. It is possible that pressure may also have a direct influence in increasing the ability of surface atoms to influence each other, thus leading to an increase in the intensity of the available cohesional forces.

With moderate pressures, the total porosity of the compact will still be considerable. The strength and hardness of the compact are results of mechanical interlocking and cold sintering and with small or moderate pressures it is probable that the latter is the major factor. However, the strength and hardness will not be large since the total area of contact is still relatively small, mainly due to unruptured oxide films and pores. In most cases, however, the strength of the compact is sufficient to allow it to be withdrawn from the mold and handled.

The most important consideration is the degree to which the particles deform, since, except for very low pressures, the degree of deformation determines the area of contact. It is well known that the softer and more plastic metals will show a greater increase of strength for a given applied pressure than the harder and more brittle metals. This is borne out in practice in that a pressure of 5 tons per square inch is hardly enough to cause tungsten particles to cohere but more than enough to form a fairly strong compact of copper or tin.

When the applied pressure is high the circumstances are different. The porosity becomes very low and mechanical interlocking probably becomes much more important than cold sintering. The fact that each particle has suffered some deformation not only throughout its volume but also by abrasion on its surface must be considered. Both of these effects result in work hardening except perhaps in certain low-melting point metals. The hardness and strength of a compact after high applied pressures is then due to complex conditions. It must be remembered, however, that the pore volume in the final stages, although becoming small, is becoming increasingly significant, since higher pressure and therefore more vigorous deformation is necessary to fill it, with a consequent greater effect on the hardness. As Jones[23] has so stated it, "the final increase in hardness, therefore, is to be regarded <u>not as a result of pressure alone</u>, but as an effect of the small but still existing porosity."

Influence of Sintering Temperature on Porosity

One of the most important variables in powder metallurgical practice is the temperature at which sintering takes place. The rate of solid diffusion is markedly influenced by temperature, so that for any given compact, the highest possible temperature should always be used. In many cases, the sintering temperature is above the melting point of one of the constituents so that a combination of sintering and impregnating takes place.

Investigators in powder metallurgy have demonstrated conclusively that variation in sintering temperature has a marked effect on the density of the compact and the nearer the sintering temperature approaches the melting point, the higher will be the density.[18] Also, not only does the higher temperature increase the rate of solid diffusion, but at the higher temperatures, the metals are more plastic and will more readily deform to fill the voids.

On raising the temperature of a metal compact, one of the first effects is a disturbance of the metal gas-vapor equilibria. These disturbances may profoundly modify the adhesive forces responsible for the sintering of the compact, and thus, it is necessary to consider the relation of a gas or vapor content of a metal powder to the final porosity. It must then be appreciated that most commercially powdered metals, especially those prepared by electrolysis, comminution of cast metals, or by reduction by a gas, contain an appreciable gas content and the liberation of these gasses on sin-

tering is beneficial from the standpoint of porosity.

There are other sources or potential sources of gas in a compressed powder compact. These are:

1. Air or other gases mechanically entrapped during compression.
2. Solid sources giving rise to gases by chemical decomposition on heating.
3. Intentionally added sources.[23]

Separately or in combination, these various sources can be responsible for large quantities of gas. The quantity of air entrapped mechanically depends mainly upon the bulking upon the bulking property of the powder. Unfavorable die conditions can greatly increase the amount of entrapped air, and in practice, attention must be paid to the clearance between the die and the plunger. This clearance must, however, be limited, otherwise air forced out of the die would carry fine powder with it. Rapid-acting presses have less tendency to entrap air than those which act slowly.[19]

Apart from solid substances that give rise to gases on heating by direct volatilization, it is necessary to consider the possibility of gas production by interaction of solid materials. Certain gas-forming reactions of this type are peculiar to powder compacts and some instances are very familiar, as for example, the "gassing" of copper by the reduction of cuprous oxide.

Other sources of gas besides those already mentioned include materials which may be added intentionally for the pur-

poses of lubrication or to promote porosity. Other solid materials may be added to gasify and eliminate certain impurities in the powder. The intentional addition of volatile substances may assist the escape of less volatile impurities and among those in common use are alkaline oxides, siliceous materials, caustic potash, sodium and potassium chloride, boric acid, sodium silicate, calcium silicate, and ammonium chloride.

This indicates that the possible sources of gas are numerous, and since apparently little is known regarding the total amounts of gas that can originate from all these sources, investigation of this phase of powder metallurgy is open for more research work.

Influence of Sintering Time.

It is difficult to differentiate between the effects produced by short time sintering at high temperatures and and long time sintering at somewhat lower temperatures. Probably the most important consideration involved in selecting a sintering time and temperature are the economics of the operation. Generally speaking, it is possible to arrive at any resultant compact condition by either high temperatures and relatively short times or by lower temperatures and and longer times and the economics of each particular operation will determine optimum conditions.

Influence of Particle Shape and Size Distribution.

The shape of the individual powder particles will vary

according to the method of manufacture, that is, powders made by the carbonyl process will be almost perfect spheres; ball-milled powders are generally thin plated of irregular outline; and powders produced by the electrolytic method are almost always dendritic. Where porosity is important, as in bearings and filters, spherical particles give the more uniform porosity and the voids produced are more uniform in size. As a result, better control can be maintained as to the percentage of voids in a compact with spherical shaped powders than with any other shape.

Theoretically, the absolute size of the particles should have no influence on the degree of porosity. However, it becomes necessary to consider certain modifications involved, especially when the particle size is made very small. The laws connecting the packing of spheres and interspace volume are independent of the size of the spheres.[29] In practice, this has been found to be far from being so, and as the particle size decreases, other influences, principally friction, either due to air or cohesion, bridging, and electrostatic effects become increasingly important. Also, the behavior of the particle is conditioned increasingly by the properties of a surface and in very fine powders the ratio between surface area and volume becomes very high.

It has been pointed out that maximum porosity is obtained when particles are of the same size and of spherical shape. If these spheres are arranged in any systematic manner of packing, there is a certain diameter ratio for a

smaller sphere which can just pass between the throats of the large spheres into the interstitial voids, thus reducing porosity. This makes the determination of the particle size distribution in a powder of paramount importance. However, since packing of the powders into a mold is generally haphazard and not systematic, no exact expression can be derived that will completely correlate screen analysis and porosity. As a result, the proper powder size distribution can be determined only after some experimental work has been done so that the range of sizes can be narrowed down considerably.

THE PROBLEM

Despite the commercial importance of powder metallurgy, not until recently has any systematic research been carried out to test some of the theories regarding the manipulation of metal powders into the finished product. Most of this research was minimized to factors essential for the perfection of a commercial product, and as a result, the scientific principles underlying this process have been sadly neglected. There is some information available, but those investigations of general interest that have been conducted are in most cases rather incomplete or not available to the public. A good illustration of this can be found in the case of the porous bearings. Although this product has been used successfully in industry during the past few years, it is extremely difficult to find any published reports on the results of investigations regarding the development of these bearings.

It is the aim of this work to establish a relationship between the variables of powder metallurgy and the porosity and oil absorption properties of the resulting compacts. The study includes a determination of the effect of variations of the following factors: compacting pressure, particle size distribution, sintering time and temperature, and heat-treating atmosphere. The tests on the compacts made include a calculation of specific gravity, percentage of voids present, oil absorbed, and percentage of voids filled.

LABORATORY EQUIPMENT

The equipment and materials used in the experimental work for this thesis consisted of:

1. Metal powders
2. Weighing and mixing apparatus
3. Pressing equipment
4. Hydrogen generator
5. Sintering furnace
6. Oil bath
7. Miscellaneous equipment

Metal Powders

The powders used were manufactured by the Metals Disintegrating Company of Elizabeth, New Jersey.

A screen analysis of these powders gave the following results:

Mesh	Copper	Tin	Graphite
100			11.7
150			33.2
200			36.2
270	12.4	3.7	14.8
-270	87.6	96.3	4.1
	100.0%	100.0%	100.0%

Weighing and Mixing Apparatus

For weighing the powder charges and the compacts, an analytical balance was used.

Thorough mixing of the powders was accomplished by the use of a tumbler mixer. This mixer consisted of a cubical box one and three quarters of an inch on each side, and made from

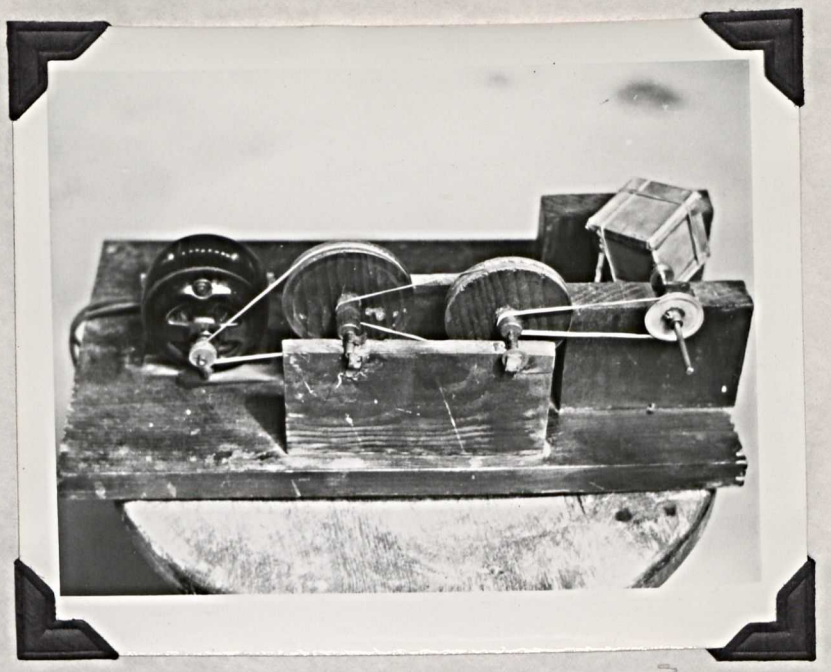

Figure 1. Mixing Apparatus

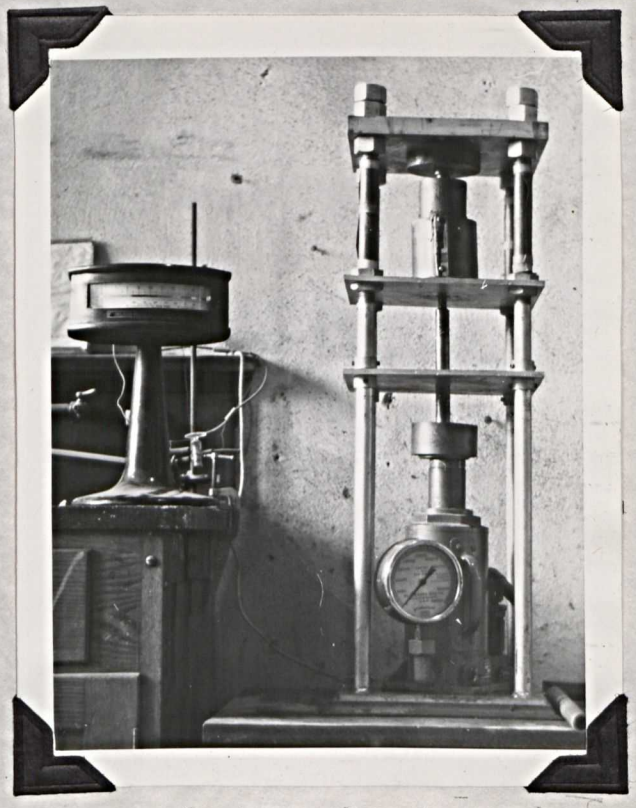

Figure 2. Pressing Apparatus
Showing Mold, Jack, and Frame.

a piece of corrosion resistant metal. The cover is fastened to the box by rubber bands, a rubber gasket preventing the fine sizes of the powder from leaking out. A steel rod, three-sixteenths of an inch in diameter, soldered through two opposite edges of the box acts as the axis of rotation.

The tumbler is connected by means of two reducing gears to a small 110-volt A.C. motor with an RPM of 1750. At this speed, centrifuging of the powders would take place, but by means of the reducing gears this is lowered to 60 revolutions per minute, at which speed very satisfactory mixing is accomplished.

Pressing Equipment

The pressing apparatus consisted of three parts: the mold, the frame, and a hydraulic jack.

The mold was machined from a heat resistant chrome steel shaft and accurately bored for the pressing and the reducing chambers, Figure 3. A heating coil is wound around the mold with an outlet so that connections can be made to the 110-volt A.C. circuit in the laboratory. By means of a system of rheostats, the current can be regulated so that pressing can be carried out at any desired temperature.

The pressing chamber is exactly one-half inch in diameter. Directly above this is the conically shaped reducing chamber with a diameter of one inch, the slant height being approximately one inch. This reducing chamber has a gas inlet and outlet, the latter being above the former so that the gas circulates upwards through the powder mixture.

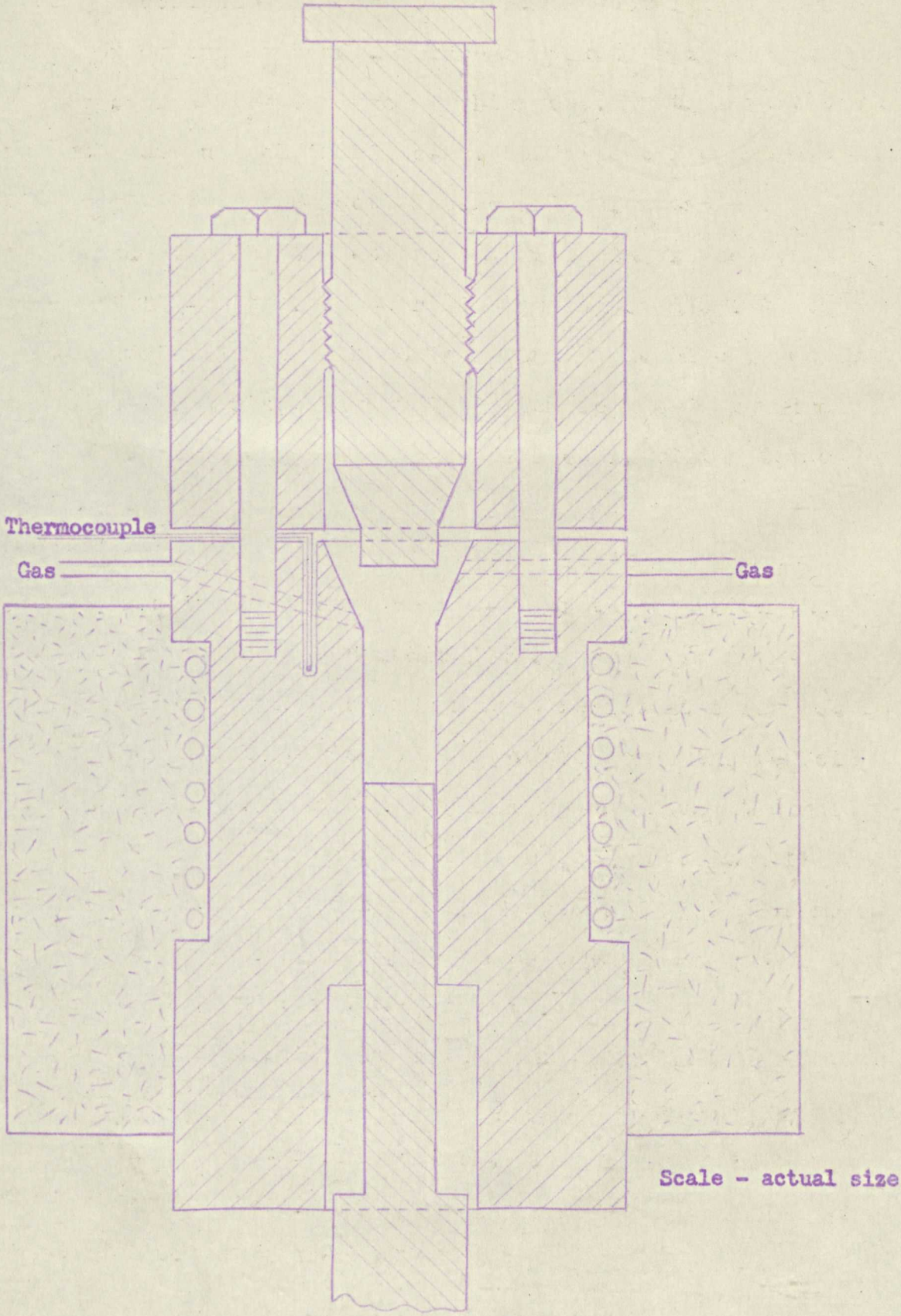

Figure 3.--Cross-section of mold.

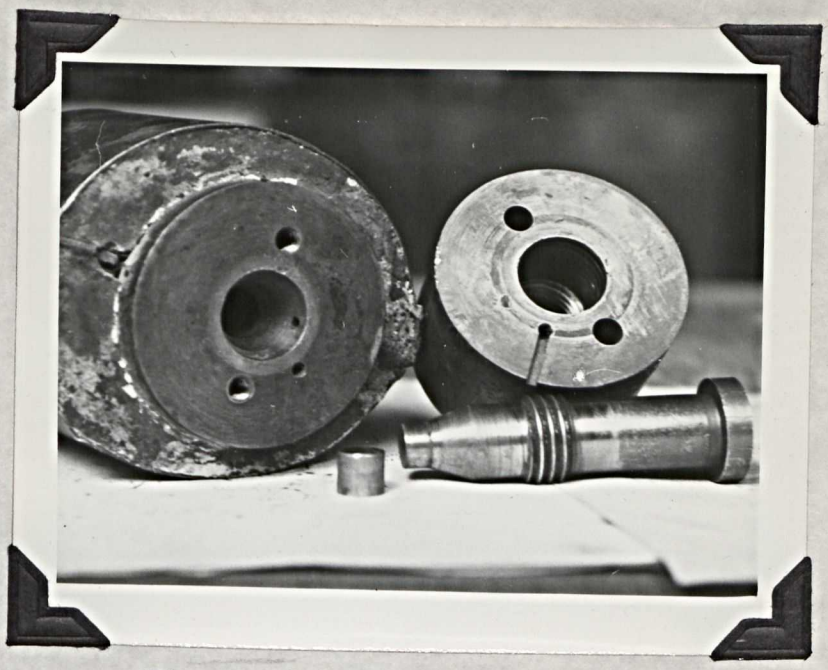

Figure 4. Component parts of mold.

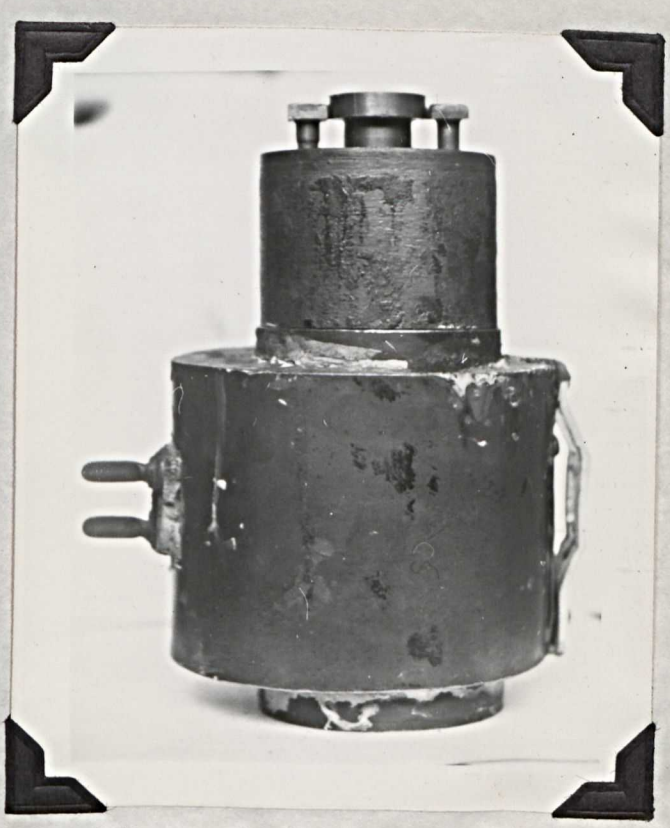

Figure 5. Mold assembled.

The cap fits on top of the mold and produces a gas tight seal for the chamber and also serves as a means for suspending the plug, the bottom of which is machined to the same angle as the flare in the gas chamber and forms the stationary end during the compression of the powders.

A chromel-alumel thermocouple inserted in a hole close to the pressing chamber measures the temperature of the mold. It is connected to a Wilson-Maulen millivoltmeter, and the actual temperature is obtained from a calibration chart.

The pressure to the ram is furnished by a Blackhawk 20-ton hydraulic jack with a safe working pressure of 40,000 pounds and a maximum pressure of 50,000 pounds per square inch, gage reading. As this gage reading gives pressure in pounds per square inch applied on a circle having a diameter of 2.562 inches, and as the ram diameter is only one half inch, the following formula is used to determine the pressure used for making the compacts:

$$\text{Tons/sq. in.} = \frac{\text{Gage reading}}{\text{area of ram in sq. in.} \times 2000}$$

The heavy steel frame, which actually receives the pressure exerted by the jack, consists of four one-inch steel rods welded to a one-inch steel base and a top of the same size steel plate against which the cap and plug are blocked. The mold rests on a quarter inch plate bored with a one-half inch hold to allow the ram to go through. Directly below this is another steel plate of the same thickness pierced in the same manner, serving as a guide for the ram.

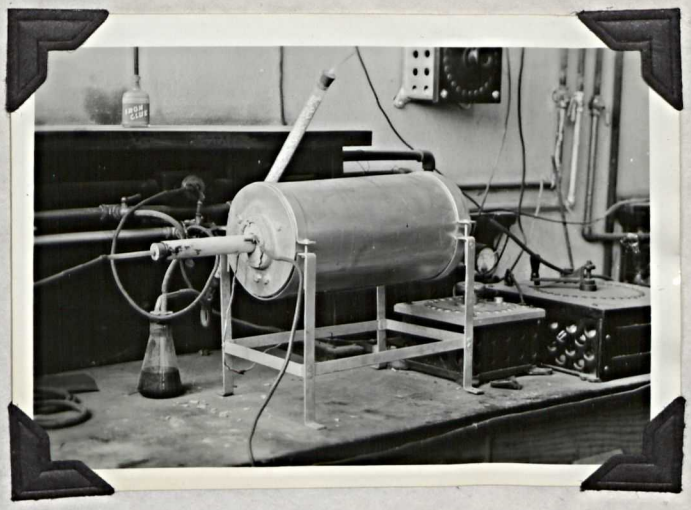

Figure 6. Sintering Furnace.

Figure 7. Oil Bath.

Hydrogen Generator.

Hydrogen was produced by the action of dilute sulphuric acid on mossy zinc which was placed in a perforated lead bucket and which could be raised or lowered into the acid to produce hydrogen gas when needed. The generator proper consisted of a liter side arm flask with a rubber stopper from which the lead bucket was suspended. From the generator, the hydrogen passed into a surge bottle to catch any acid that might be forced backward by accidental reversed pressure. From here, it bubbled through alkaline pyrogallic acid to remove any oxygen present. It then passed through another surge bottle and then into concentrated sulfuric acid to remove moisture. To insure complete dryness the hydrogen was then passed through calcium chloride and calcium sulfate.

Sintering Furnace.

A laboratory tube furnace was used to heat-treat the compacts. It had a maximum operating temperature of 1000°C. and a safe working temperature of from 800 to 900°C. Current was obtained from the 110-volt A.C. line. The amperage flowing through the furnace was controlled by two rheostats connected in series. Iron-constantan thermocouples, connected to a millivoltmeter, were calibrated to indicate the furnace temperature.

Oil Bath

The oil used was S.A.E.#20. It was placed in a small tin dish and the compacts were introduced into this oil bath.

Miscellaneous Equipment.

Lubriplate was used to lubricate the sides of the pressing chamber as well as the ram. The use of this lubricant facilitated the removal of the compacts from the mold, especially where the higher compacting pressures were used.

Linear dimensions of the compacts were obtained by calipers and the volume was calculated from these dimensions.

A laboratory hot plate was used for keeping the oil bath and the pickling solution at constant temperature.

EXPERIMENTAL PROCEEDURE

Due to the extensive nature of the investigation, it was necessary to limit the work to one definite composition, and the composition finally chosen was 88 per cent copper, 11 per cent tin, and 1 per cent graphite, which is essentially that used in the commercial porous bearings.

The powders were weighed in batches of 100 grams of the composition chosen, and then placed in the tumbler mixer. After a period of fifteen minutes, the powders were thoroughly mixed. From this batch, three 10-gram and three 11-gram samples were weighed. These formed the charges to the pressing mold, the 10-gram samples being used at the lower pressures while the 11-gram samples were used at the higher pressures. This was done to obtain compacts of approximately the same length.

These six samples from the mixed powders made the six compacts in each series. The compacting pressures used are as follows: 6.4, 12.8, 19.2, 25.6, 32.0, and 38.4 tons per square inch. The compacts, on removal from the mold were consolidated enough to be handled easily. Their dimensions and weight were taken and the percentage of voids present was calculated by the following method:

$$\frac{\text{Volume in cc. of compact}}{\text{Weight in grams}} = \text{actual specific gravity}$$

$$\frac{88}{8.92} = 9.86 \text{ cc. of Cu}$$

$$\frac{11}{7.31} = 1.51 \text{ cc. of Sn}$$

$$\frac{1}{2.25} = 0.39 \text{ cc. of C}$$

$$11.76 \text{ cc. of alloy}$$

Since 100 grams of this alloy occupies 11.76 cc., then the theoretical specific gravity of a compact of this composition with no voids would be $\frac{100}{11.76} = 8.50$, so that

$$100 - \frac{\text{actual specific gravity}}{\text{theoretical specific gravity}} \times 100 = \text{per cent voids}$$

The compacts were then heat-treated and then placed in the oil bath which was kept at a constant temperature of 60°C. The specific gravity of the oil was found to be 0.85. The volume of oil absorbed, after an immersion of 24 hours, was then determined in this manner:

$$\frac{\text{grams of oil absorbed}}{\text{specific gravity of oil}} = \text{volume in cc. of oil absorbed}$$

$$\frac{\text{vol. in cc. of oil}}{\text{vol. of compact}} = \text{per cent volume of compact occupied by the oil}$$

After this 24-hour immersion, the compacts were dried and then given a pickling treatment for 15 minutes in a 20% solution of sulphuric acid at 85°C. They were then washed in water, dried, and again put back into the oil bath for another 24-hour period.

To examine the effects of variables such as compacting pressure, particle size distribution, sintering time, and sintering atmosphere and temperature, six series of compacts were made. These were:

1. Series 1. Compacts of -270 mesh powders. Heat-treated at 600°C. for 30 minutes and then air cooled. Immersed in the oil bath for 24 hours, pickled, and then put back into the oil bath for another 24 hours.

2. Series II. Compacts made from the powders as received from the manufacturer, i.e., with the range of particle sizes as shown in the screen analysis. After compression, they were pickled, heat-treated, and then immersed in the oil bath for 24 hours. They were then pickled and then returned to the oil bath for another 24 hours.

3. Series III. Compacts made from unsized powders, heat-treated at 600°C. for two hours and then furnace cooled. Then the proceedure as in Series II was followed.

4. Series IV. Compacts of plus 270 mesh powders, followed by the same proceedure used for Series III.

5. Series V. Compacts of -270 mesh powders, followed by the same proceedure as for Series III.

6. Series VI. Compacts made from unsized powders, heat-treated at 800°C. for thirty minutes, followed by method used for Series III.

These variables are summed up as follows:

1. Pressure: compacts were made at 6.4, 12.8, 19.2, 25.6, 32.0, and 38.4 tons per square inch.

2. Particle size distribution: compacts made from the powders as received from the manufacturer so as to include the size distribution shown in the screen analysis; compacts of plus 270 mesh powders; compacts of minus 270 mesh powders.

3. Sintering temperature and time: 600°C. for 30 minutes and air cooled, 600°C. for 2 hours and furnace cooled, and 800°C. for thirty minutes and air cooled.

4. Sintering atmosphere: reducing.

Series I

Compacts of -270 mesh powders, heat-treated at 600°C. for 30 min. and air cooled.

Unsintered

Pressure tons/sq. in.	Weight grams	Volume c.c.	Specific gravity	Per cent voids
6.4	10.01	1.94	5.22	38.5
12.8	9.95	1.68	5.92	30.5
19.2	9.87	1.51	6.53	23.3
25.6	10.90	1.55	7.04	17.3
32.0	7.65	1.04	7.35	13.6
38.4	10.97	1.48	7.40	13.0

Table 1. The effect of pressure on specific gravity and per cent voids.

Sintered

Pressure tons/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.72	1.85	5.25	38.3
12.8	9.91	1.65	6.00	29.3
19.2	9.83	1.52	6.46	24.0
25.6	10.82	1.59	6.82	19.8
32.0	7.61	1.07	7.12	16.3
38.4	10.90	1.51	7.22	15.0

Table 2. The effect of sintering on specific gravity and per cent voids.

	Before pickling		After pickling		
Pressure	Vol. oil absorbed	Per cent compact vol.	Vol. oil absorbed	Per cent compact vol.	Per cent voids filled
6.4	.63	34.0	.61	37.1	97.0
12.8	.40	24.0	.47	28.2	96.3
19.2	.24	15.8	.30	19.6	81.6
25.6	.20	12.7	.26	16.7	84.3
32.0	.08	7.7	.15	14.1	86.5
38.4	.01	0.7	.13	8.6	57.3

Table 3. The effect of pickling and pressure on per cent volume of oil absorbed and on voids filled.

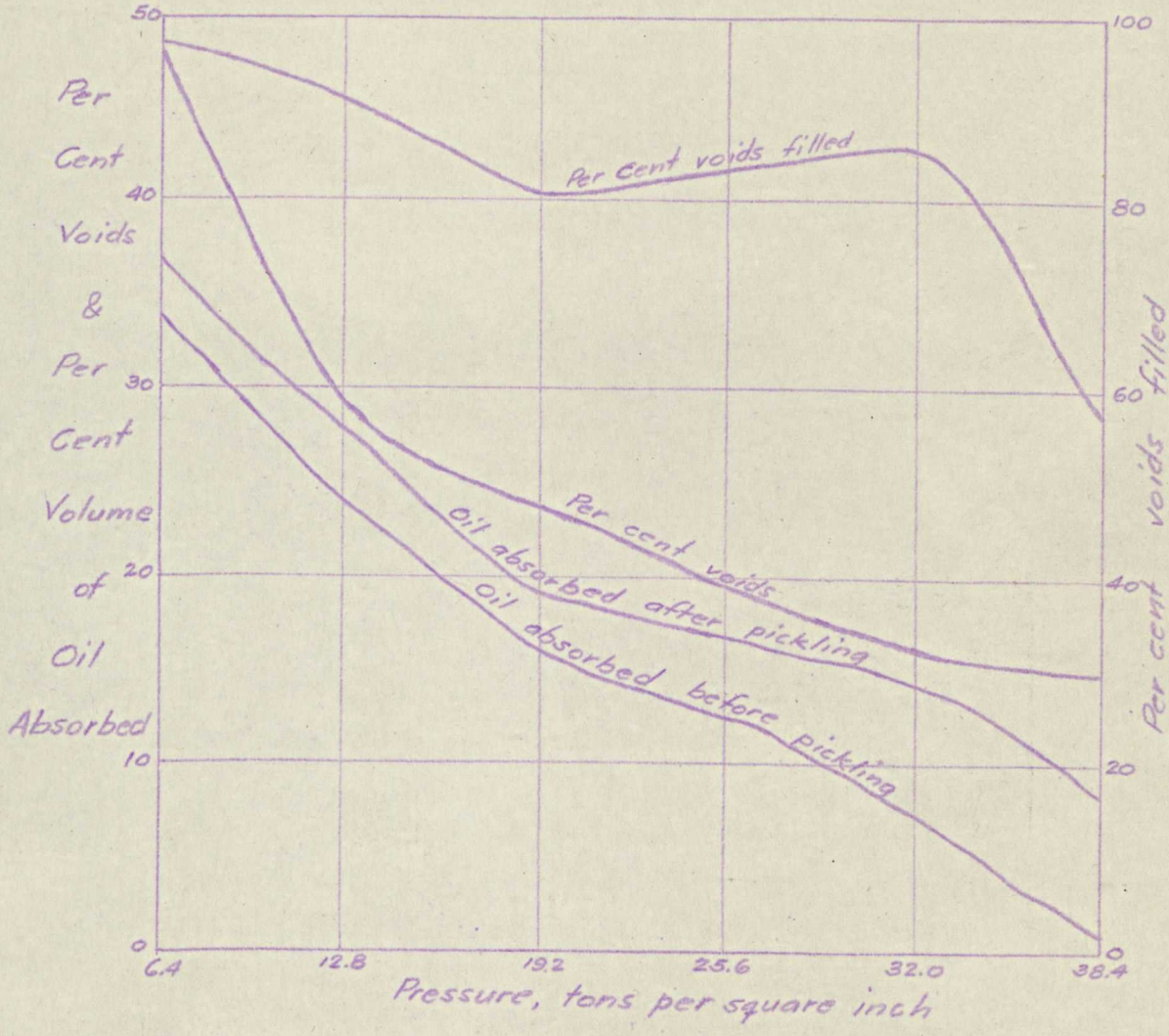

Figure 7.--Effect of pressure on per cent voids and volume of oil absorbed for compacts of Series I.

Series II

Compacts pickled and then heat-treated at 600°C. for 30 min. and air cooled.

Unsintered

Pressure tons/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.92	2.00	4.96	41.7
12.8	9.90	1.70	5.82	31.7
19.2	9.95	1.53	6.50	23.5
25.6	10.86	1.57	6.92	18.5
32.0	10.83	1.51	7.18	15.5
38.4	10.88	1.48	7.35	13.6

Table 4. The effect of pressure on specific gravity and per cent voids.

Sintered

Pressure ton/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	10.11	2.06	4.92	42.2
12.8	10.04	1.76	5.93	30.2
19.2	10.00	1.65	6.05	28.8
25.6	10.80	1.64	6.60	22.3
32.0	10.74	1.60	6.72	21.0
38.4	10.80	1.53	7.08	16.7

Table 5. The effect of sintering on specific gravity and per cent voids.

	Before pickling		After pickling		
Pressure	Vol. oil absorbed	Per cent compact vol.	Vol. oil absorbed	Per cent compact vol.	Per cent voids filled
6.4	.75	36.6	.85	41.2	97.5
12.8	.47	26.8	.48	27.2	90.0
19.2	.35	21.0	.35	21.0	73.0
25.6	.32	19.8	.32	19.8	88.7
32.0	.26	16.3	.29	18.4	87.5
38.4	.22	14.6	.24	15.7	94.0

Table 6. The effect of pickling and pressure on per cent volume of oil absorbed and on voids filled.

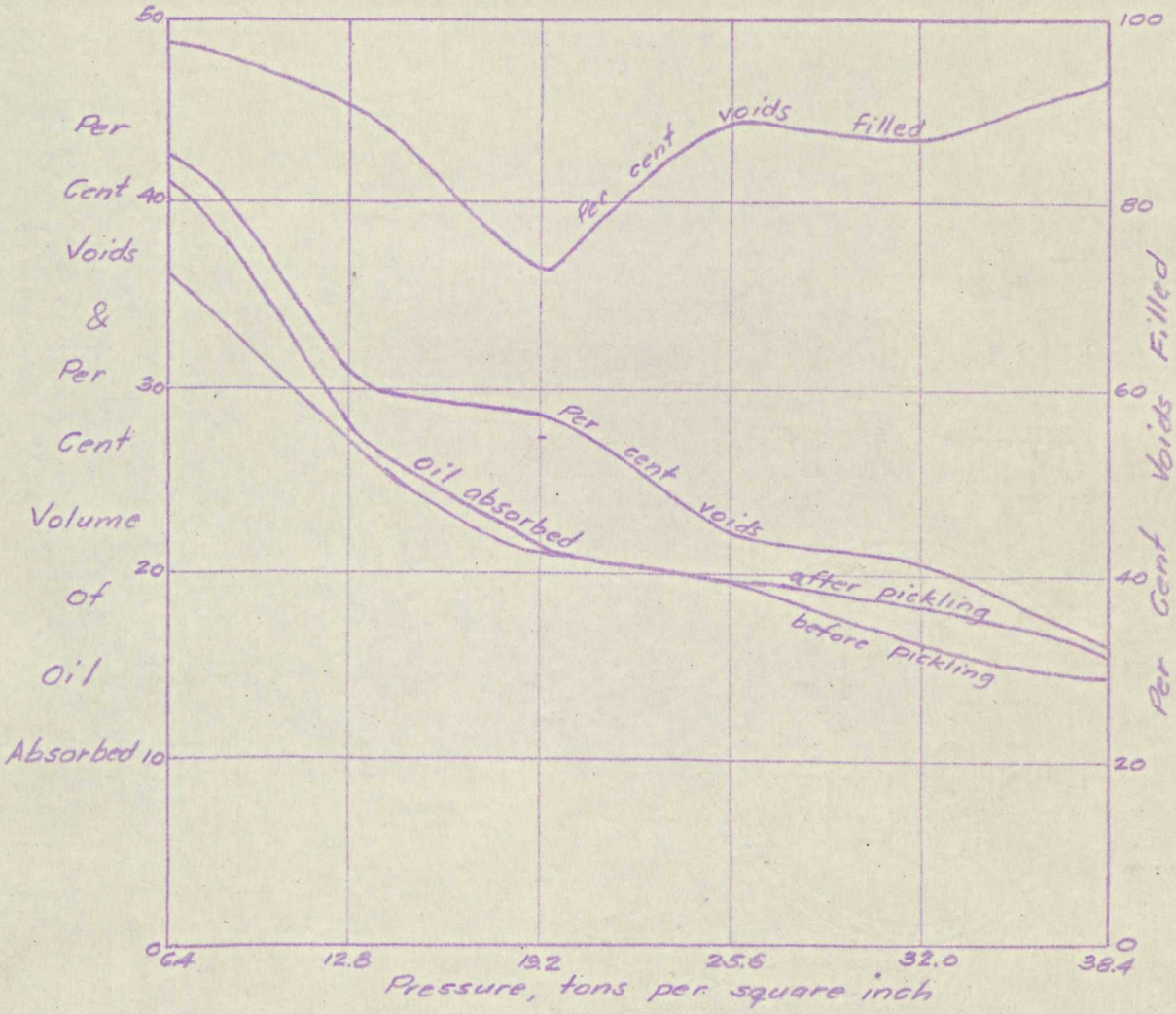

Figure 8.--Effect of pressure on per cent voids and volume of oil absorbed for compacts of Series II.

Series III

Compacts heat-treated at 600°C. for 2 hours and furnace cooled.

Unsintered

Pressure tons/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.83	1.99	4.95	41.8
12.8	9.92	1.71	5.79	31.8
19.2	9.91	1.54	6.44	24.2
25.6	10.91	1.58	6.91	18.7
32.0	10.94	1.52	7.20	15.3
38.4	10.90	1.47	7.40	13.0

Table 7. The effect of pressure on specific gravity and per cent voids.

Sintered

Pressure tons/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.75	1.96	4.97	41.5
12.8	9.86	1.68	5.87	30.9
19.2	9.85	1.50	6.55	22.9
25.6	10.84	1.50	6.75	20.6
32.0	10.86	1.61	7.23	18.3
38.4	10.82	1.70	7.42	14.8

Table 8. The effect of sintering on specific gravity and per cent voids.

	Before pickling		After pickling		
Pressure	Vol. oil absorbed	Per cent compact vol.	Vol. oil absorbed	Per cent compact vol.	Per cent voids filled
6.4	.67	34.2	.80	40.9	98.5
12.8	.38	22.8	.44	26.2	85.0
19.2	.18	17.8	.25	16.8	73.5
25.6	.09	5.9	.14	9.4	45.6
32.0	.06	4.0	.08	5.0	27.6
38.4	.05	3.1	.09	5.2	35.2

Table 9. The effect of pickling and pressure on per cent volume of oil absorbed and on voids filled.

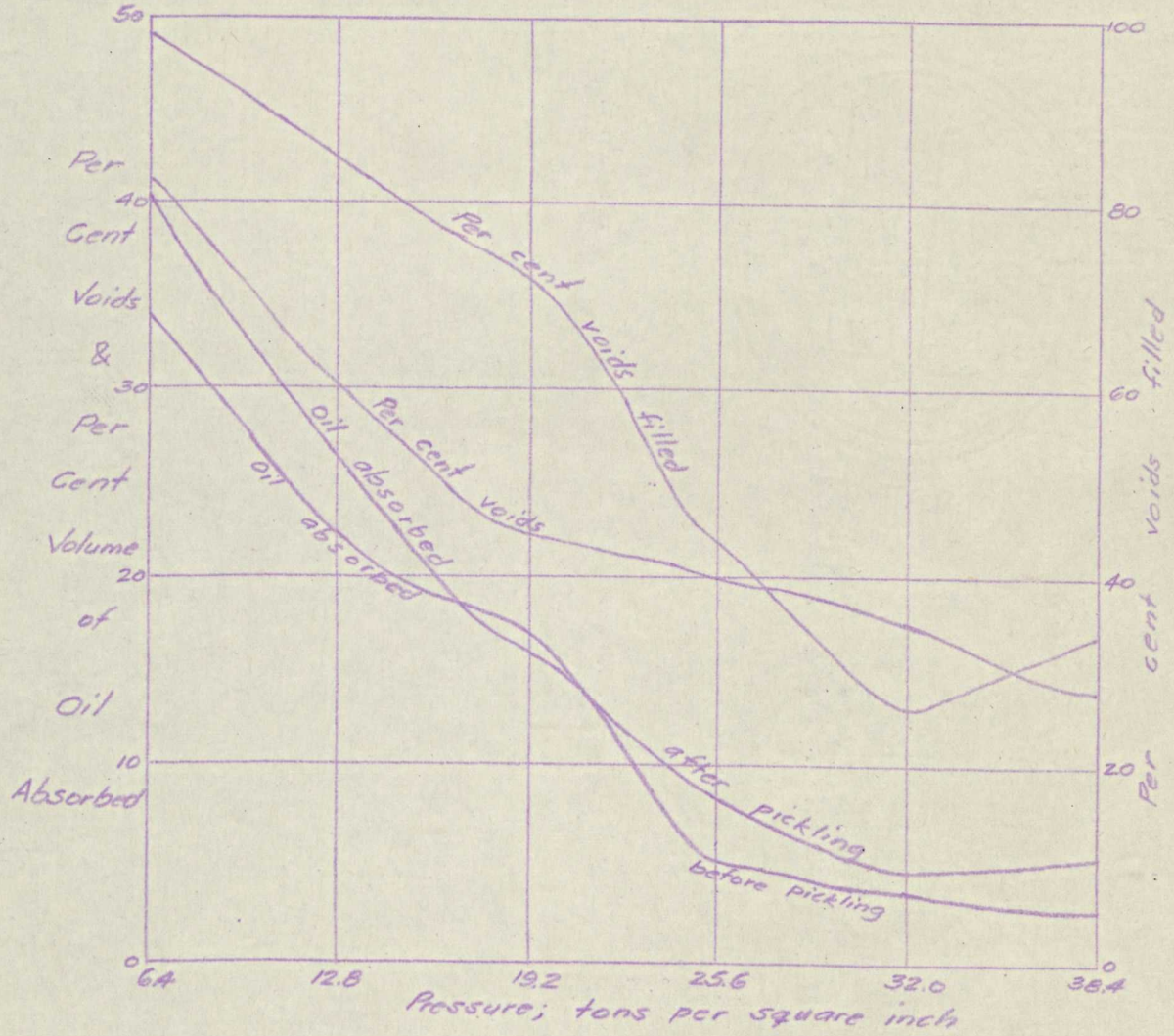

Figure 9.--Effect of pressure on per cent voids and volume of oil absorbed for compacts of Series III.

Top

Series lV

Compacts of + 270 mesh powders, heat-treated at 600°C. for two hours anf furnace cooled.

Unsintered

Pressure tons/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.95	1.98	5.02	41.0
12.8	9.98	1.64	6.08	28.5
19.2	9.98	1.52	6.56	22.8
25.6	10.97	1.58	6.86	18.2
32.0	10.92	1.52	7.20	14.3
38.4	10.90	1.47	7.42	12.8

Table 10. The effect of pressure on specific gravity and per cent voids.

Sintered

Pressure tons/ sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.88	1.95	5.06	40.4
12.8	9.92	1.72	5.76	32.2
19.2	9.92	1.59	6.23	26.7
25.6	10.89	1.67	6.52	23.2
32.0	10.85	1.58	6.86	19.3
38.4	10.81	1.59	6.80	20.0

Table 11. The effect of sintering on specific gravity and per cent voids.

	Before pickling		After pickling		
Pressure	Vol. oil absorbed	Per cent compact vol.	Vol. oil absorbed	Per cent compact vol.	Per cent voids filled
6.4	.52	26.4	.82	41.8	----
12.8	.36	17.8	.52	30.2	93.7
19.2	.20	12.6	.32	20.8	76.0
25.6	.21	12.4	.33	19.7	84.9
32.0	.15	17.2	.24	15.6	81.0
38.4	.15	9.5	.23	14.4	72.0

Table 12. The effect of pickling and pressure on per cent volume of oil absorbed and on voids filled.

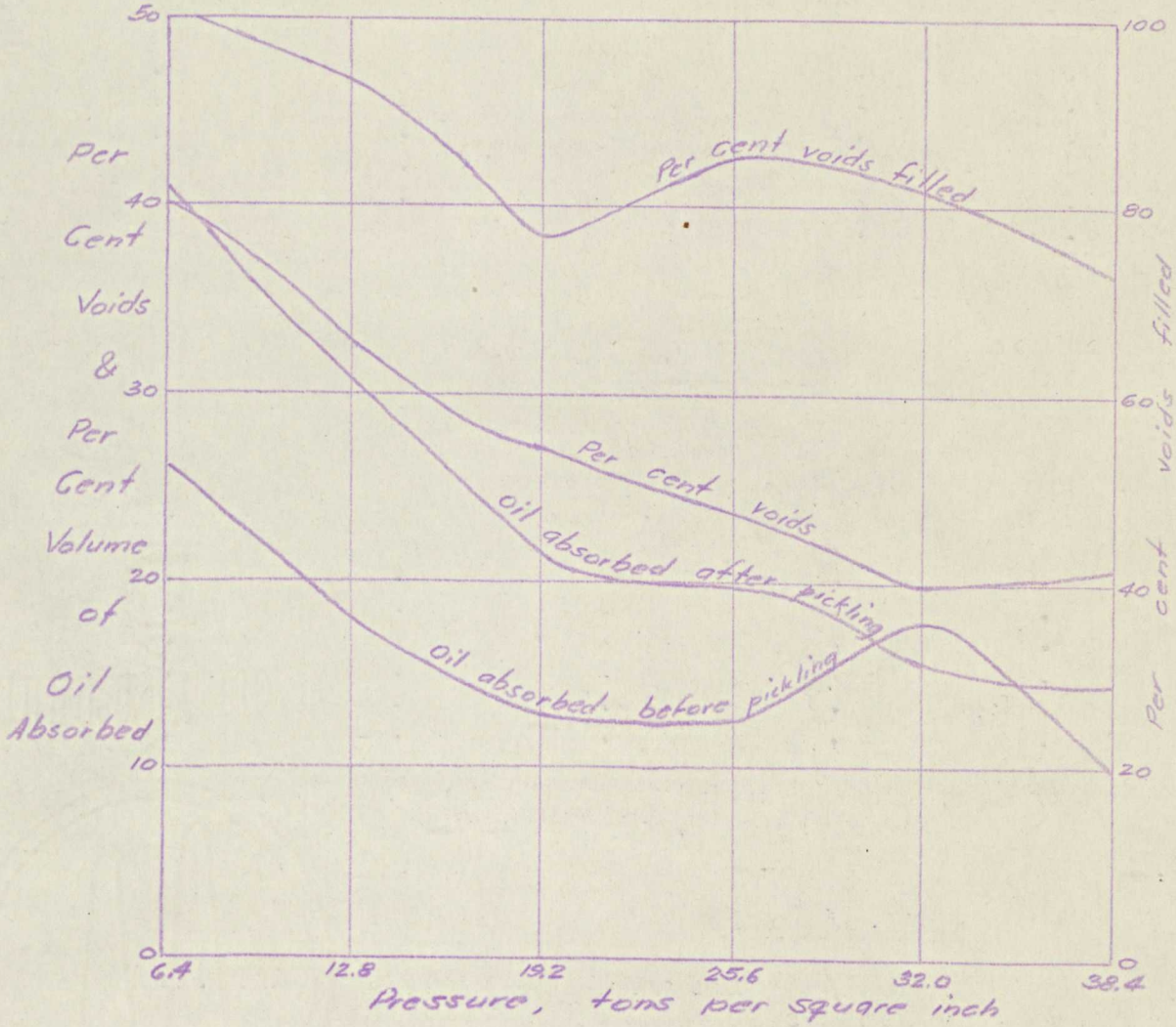

Figure 10.--Effect of pressure on per cent voids and volume of oil absorbed for compacts of Series IV.

Series V

Compacts of — 270 mesh powders, heat-treated at 600° C. for two hours and furnace cooled.

Unsintered

Pressure tons/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.73	1.98	4.90	42.3
12.8	9.91	1.64	6.03	29.0
19.2	9.86	1.49	6.62	22.0
25.6	10.62	1.53	7.10	16.5
32.0	10.86	1.48	7.35	13.7
38.4	10.88	1.47	7.40	13.0

Table 13. The effect of pressure on specific gravity and per cent voids.

Sintered

Pressure tons/sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.65	1.90	5.07	40.4
12.8	9.83	1.61	6.10	28.2
19.2	9.79	1.46	6.70	21.0
25.6	10.78	1.50	7.18	15.5
32.0	10.78	1.53	7.05	17.0
38.4	10.80	1.53	7.05	17.0

Table 14. The effect of sintering on specific gravity and per cent voids.

	Before pickling		After pickling		
Pressure	Vol. oil absorbed	Per cent compact vol.	Vol. oil absorbed	Per cent compact vol.	Per cent voids filled
6.4	.62	32.6	.76	40.0	99.0
12.8	.29	18.3	.41	25.6	90.6
19.2	.13	8.8	.25	16.9	80.5
25.6	.09	6.1	.12	8.4	54.2
32.0	.07	4.5	.09	6.3	37.0
38.4	.06	3.9	.07	4.8	28.0

Table 15. The effect of pickling and pressure on per cent volume of oil absorbed and on voids filled.

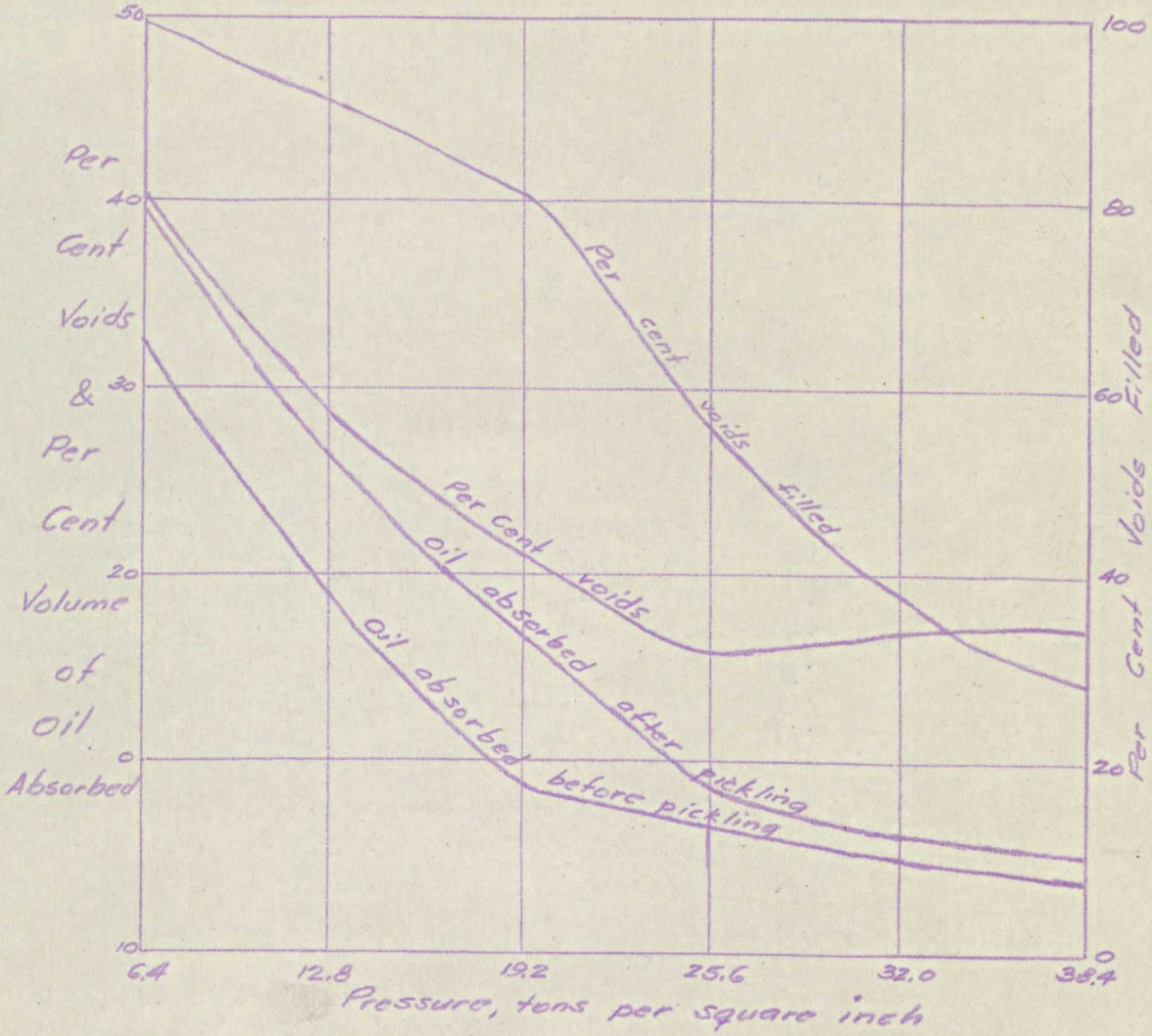

Figure 11.--Effect of pressure on per cent voids and volume of oil absorbed for compacts of Series V.

Series V1

Compacts heat-treated at 800°C. for two hours and air cooled.

Unsintered

Pressure tons/ sq. im.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.85	1.98	4.97	41.5
12.8	9.91	1.67	5.92	30.4
19.2	9.88	1.52	6.50	23.6
25.6	10.82	1.54	7.04	17.3
32.0	10.81	1.49	7.25	14.8
38.4	10.85	1.47	7.38	13.2

Table 16. The effect of pressure on specific gravity and per cent voids.

Sintered

Pressure tons/ sq. in.	Weight grams	Volume cc.	Specific gravity	Per cent voids
6.4	9.42	1.29	7.25	14.8
12.8	10.10	1.63	6.20	27.0
19.2	9.45	1.49	6.35	24.5
25.6	10.72	1.69	6.35	24.5
32.0	10.27	1.64	6.25	26.5
38.4	10.87	1.71	6.35	24.5

Table 17. The effect of sintering on specific gravity and per cent voids.

	Before pickling		After pickling		
Pressure	Vol. oil absorbed	Per cent compact vol.	Vol. oil absorbed	Per cent compact vol.	Per cent voids filled
6.4	.15	11.4	.16	12.8	85.3
12.8	.22	13.3	.28	17.2	63.8
19.2	.27	18.1	.31	20.8	85.0
25.6	.31	18.4	.35	20.6	84.0
32.0	.27	16.3	.28	17.2	65.0
38.4	.24	14.5	.27	15.8	64.5

Table 18. The effect of pickling and pressure on per cent volume of oil absorbed and on voids filled.

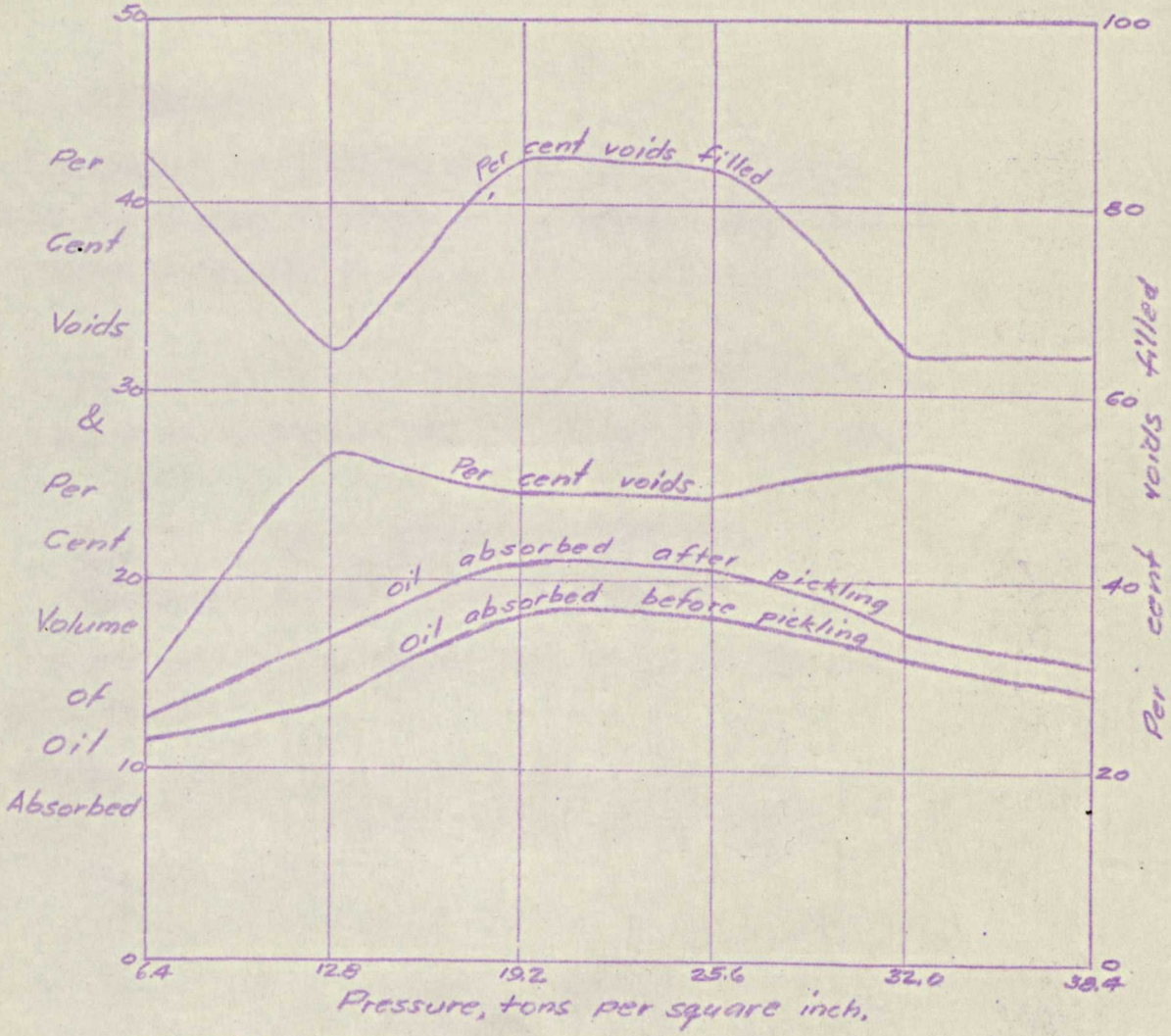

Figure 12.--Effect of pressure on per cent voids and volume of oil absorbed for compacts of Series VI.

DISCUSSION OF RESULTS

The most noticeable result of the tests performed on the compacts was that porosity was decreasingly reduced as the compacting pressure was increased. The increment in pressure was constant, that is, 6.4 tons per square inch for every succeeding compact made, while the decrease in porosity was also constant so that when one was plotted against the other, the resulting graph approached a straight line. The percentage of voids could be easily reproduced for compacts made at the same compacting pressure. With the decrease in porosity, there was, naturally, an increase in the specific gravity. However, the relation of specific gravity to pressure was not as clear cut or could it be predetermined as in the case of porosity.

Hall[18] states that products of this composition attain their maximum density at temperatures around 810°C. for a sintering schedule of 30 minutes, and that under these conditions of heat treatment, alloying of the copper and tin is complete. An examination of the compacts produced in Series VI which were heat-treated at 800°C. for 30 minutes confirmed the above observation. Under the microscope, these compacts showed golden colored alpha bronze as the predominant constituent. Except for the first compact, the other five in the series approached a constant specific gravity of 6.30 and a porosity of 25 per cent.

Compacts heat treated at 600°C. for 30 minutes did not show complete alloying. The tin had all melted to form an

intercommunicating structure around the bronze grains. On the other hand, the compacts sintered at 600°C. for 2 hours and then furnace cooled, showed complete alloying and with a structure similar to that obtained in the compacts sintered at 800°C. for 30 minutes. This is a good illustration of the theory that a long time heat treatment at low temperature will give the same result as a short time sinter at high temperature.

The pickling treatment increased the oil absorption properties of all the compacts. No doubt, during the pressing operation and the subsequent removal of the compact from the mold, a layer of deformed metal was produced so as to seal off some of the voids. The pickling treatment simply etched the surface and uncovered some of these voids. This is seen quite clearly in the products of Series II which were given this treatment before sintering. On immersion in the oil bath, pickled, and then immersed again, only a very slight increase in oil absorption was obtained, which seems to indicate that once the voids are uncovered, they tend to remain uncovered even during the sintering operation when the tin is in a molten state.

Another important effect of this pickling treatment before sintering is that, with the voids uncovered, the hydrogen gas used in the furnace was able to permeate through the body of the compact easier, with the result that a better reductuon of the oxide coating was obtained, so that more

complete alloying was noticeable than in the compacts of Series I which were heat-treated under identical conditions.

A comparison of the results obtained for Series IV, that is, of compacts made from plus 270-mesh powders, with that of Series V, minus 270-mesh powders, shows clearly the effect of particle size distribution, which substantiates the theory that the smaller particles tend to fill up the interstices between the larger particles. This is evident in the calculated percentage of voids present as well as in the oil absorption properties of the two series, that of the sized particles being the better of the two.

As the work was done with powders bought from a manufacturer, there was no control over particle shape. A microscopic examination of the powders showed them to be of irregular shape, dendritic in most cases. No doubt the oil absorbing qualities of the compacts produced could be increased if powders of spherical shape were used. The use of such powders, if available, is suggested for future work on porosity studies.

CONCLUSIONS

From the tests performed on the compacts, the following conclusions have been drawn: High compacting pressures give the highest densities and, as a result, give the lowest percentage of porosity and oil absorption qualities; the closer the sintering temperature approaches the melting point, the less the porosity; a short sintering period at high temperature is equivalent to a long sintering treatment at low temperature.

The fact that a pickling treatment increased the oil absorbing qualities of the compacts showed that some of the voids were covered and that the removal of this layer of deformed metal that enclosed the compacts, increased their oil absorbing properties, this increase being almost double in some cases.

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